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Final Report
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Project Title: **Theoretical Studies of Rate Coefficients for Gas Phase Reactions**

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Project Summary

This project was concerned with the theoretical description of two classes of gas phase chemical reactions: (1) reactions involved in the formation and removal of NO_x in combustion systems, and (2) reactions involved in the production of soot precursors starting from acetylene.

Our work on NO_x reactions was primarily concerned with reactions which sample the HNNO potential surface, namely

$$NH + NO \rightarrow H + N_2O$$
$$\rightarrow N_2 + OH$$

and the reverse

$$H + N_2O \rightarrow N_2 + OH$$
$$\rightarrow NH + NO$$
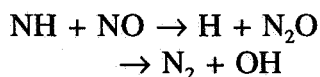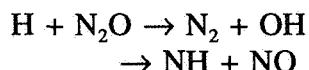
In the previous year of our NASA Ames work, we developed an empirical potential surface for HNNO, using comparisons with *ab initio* calculations to refine stationary points and reaction paths. Extensive quasiclassical trajectory (QCT) studies of the NH + NO reaction were completed early this year, and subsequently we performed RRKM studies of NH + NO, and QCT studies of $H + N_2O$. Further studies aimed at modelling the van der Waals precursor variant of $H + N_2O$, namely $HBr \cdot N_2O + h\nu \rightarrow$ products are underway.

Among highlights of these studies are the following:

(1) Both QCT and RRKM results show that the branching fraction in the NH + NO reaction is 10-15% to produce $N_2 + OH$ products. There was significant controversy concerning the

correct value of this fraction when we first generated it, but several new measurements within the past year have produced results which agree with our estimate to within a factor of two. Estimates we made of the sensitivity of our results to possible errors in the potential surface are consistent with the factor of two maximum deviation. We also demonstrated that RRKM theory is reliable for determining branching behavior for reactions like NH + NO where the intermediate complex lifetime is only 0.5 ps.

(2) Our QCT studies of H + N_2O have demonstrated that the highly curved Arrhenius plots seen in recent kinetics measurements may be rationalized in terms of contributions from two different pathways for reaction to produce the N_2 + OH product. These pathways involve attack of the H atom on either end of N_2O, with N-atom attack leading to intermediate complex formation, while O-atom attack is direct. Prior work had only considered one pathway (N-attack), and had assumed that the curvature was either due to pressure effects or to tunnelling. Neither of the earlier mechanisms were able to generate results that tied together experiment and *ab initio* properties consistently.

(3) Our QCT studies of H + $N_2O \rightarrow N_2$ + OH have cast doubt on measurements of product energy partitioning measurements from Wittig's group, and this in turn influences the interpretation of the reaction mechanism in femtosecond measurements. Wittig's group assumes that N-atom attack is dominant at high energies and that this gives significant N_2 vibrational and rotational excitation. We find that O-atom attack is more important, and that attack on either end gives little N_2 vibrational excitation.

Another project was concerned with understanding reactions important in the production of soot precursor molecules (i.e., molecules that can react to form polycyclic aromatic hydrocarbons). The specific reactions of most interest to this study have been the reactions of CH and $^1CH_2$ with acetylene, as these provide pathways for propargyl radical formation, and propargyl can dimerize to produce C_6 aromatics. Here we have used variational RRKM methods to calculate the reaction rates and intermediate complex lifetimes. Transition state properties have been taken from Walch's calculations. Our calculations are still incomplete, but what we have done so far indicates that CH + C_2H_2 is a fast reaction (k ~ 6 x 10^{-10} cm^3/s), with weak temperature dependence. Intermediate complex lifetimes are short (few ps) so at pressures below atmospheric, H + CH_2CC should be the dominant product. Our studies of $^1CH_2$ + C_2H_2 are also incomplete, but this appears to be a slower reaction than CH + C_2H_2) that produces long-lived intermediates (propyne and allene). At sufficiently high pressures, propyne and allene should be dominant over propargyl + H as the final product.

Research Summary

Students supported: Kim Bradley/ Renee Guadagnini

I. Introduction

This is the final report for NASA Ames grant NCC 2-774. The research involved theoretical studies of elementary chemical reactions that are important in atmospheric and combustion chemistry, especially those which involve the formation and removal of NO_x, and those which involve the formation of soot precursor molecules. Many of these reactions are difficult to study using conventional gas phase kinetics experiments because they involve radicals that are hard to prepare or detect, so we have used theory as an alternative to experiment in determining the relevant kinetics information. The theoretical calculations involved two steps: first the potential energy surfaces which determine the forces between the atoms during reaction were determined, and second these surfaces were used to simulate reactions, extracting relevant kinetics information from the results. This research program thus sought to use high quality theoretical methods to provide new kinetics information that is important in understanding the combustion of hydrocarbons and nitrogen containing fuels.

II. Summary of Progress to Date (since 11/94)

Papers:

Global Potential Energy Surfaces for the Lowest $^1A'$, $^3A''$ and $^2A''$ States of HNO, R. Guadagnini, G. C. Schatz and S. P. Walch, J. Chem. Phys., **102**, 774-83 (1995).

Quasiclassical Trajectory Studies of N + OH, O + NH and H + NO Collisions using Global *Ab Initio* Potential Energy Surfaces," R. Guadagnini, G. C. Schatz, and S. P. Walch, J. Chem. Phys., **102**, 784-91 (1995).

Quasiclassical Trajectory Studies of State Resolved Bimolecular Reactions: Vibrational Distributions in Triatomic Products, G. C. Schatz, J. Phys. Chem., **99**, 516-24 (1995).

A Theoretical Study of the NH + NO Reaction, K. S. Bradley, P. McCabe, G. C. Schatz, and S. P. Walch, J. Chem. Phys., **102**, 6696-705 (1995).

RRKM Studies of Product Branching in the NH + NO Reaction, M. Simonson, K. S. Bradley and G. C. Schatz, Chem. Phys. Lett. **244**, 19-26 (1995).

Mode-specific Chemistry in the H + HCN and H + N_2O Reaction, M. ter Horst, K. S. Bradley and G. C. Schatz, in *Gas Phase Chemical Reaction Systems: Experiments and Models 100 Years After Max Bodenstein*, proceedings of symposium in honor of Max Bodenstein, Ed. H. -R. Volpp and J. R. Wolfrum, Springer, Berlin, 1996, in press.

A Quasiclassical Trajectory Study of H + $N_2O(v_1,v_2,v_3)$, K. S. Bradley and G. C. Schatz, J. Phys. Chem., submitted.

(1) The H + N_2O and NH + NO Reactions

One component of our research program this year was concerned with reactions that are associated with the HNNO potential surface, namely

$$NH + NO \rightarrow OH + N_2 \quad (1a)$$

$$\rightarrow H + N_2O \quad (1b)$$
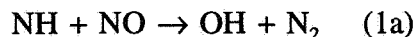
and the reverse reactions:

$$H + N_2O \rightarrow OH + N_2 \quad (2a)$$

$$\rightarrow NH + NO \quad (2b)$$

Reactions 1a and 1b are important[1,2] in thermal De-NO_x, with 1b providing one of the dominant pathways for the production of N_2O. Reaction (2b) is part of the "N_2O mechanism" for NO production in hydrocarbon flames[1]. An important parameter in the modelling of NH + NO is the branching ratio between 1a and 1b. The measured values for this branching ratio show wide variation, ranging from 100% 1a (from Okada and coworkers[3]) to 0% 1a[4] (both at 300K), and from 19% to 32% 1a[5] (under shock tube conditions).

Recent interest in reactions (2a-2b) comes from several reaction dynamics experiments[6,7], including a novel study by Wittig and coworkers[6] in which UV photolysis of the van der Waals precursor HBr-N_2O results in the intramolecular version of (2a) and (2b). These experiments show that branching between (2a) and (2b) can be altered by causing the reaction to occur in a van der Waals cluster rather than in the bulk. In addition, femtosecond pump-probe experiments[8] indicate that (2a) occurs on a time scale of less than 100fs, which is in contrast to the isoelectronic reaction H + CO_2 → OH + CO in which a HOCO intermediate complex is formed with a 0.5ps lifetime.

Reaction 2a is also interesting because kinetics measurements[9-11] show unusual temperature dependence to the bimolecular rate constant, with an activation energy that increases rapidly with temperature. Several attempts at modelling these results have failed to explain all the experiments. Marshall et al[9] have argued that the strong temperature dependence arises from unusually large contributions from tunnelling at low temperatures, but they were unable to quantitatively model their measured results. Diau and Lin[10] and Bozzelli et al[11] have successfully fit the same data using an approximate RRKM model where pressure-dependent effects rather than tunnelling are responsible for the strong temperature dependence of the rate constant. However their results predict a strong pressure dependence to the results that does not match the experiments.

Walch[12] has recently characterized all the kinetically important stationary points on the two lowest potential surfaces ($^2A'$ and $^2A''$) of HNNO. His results do not completely agree with earlier calculations[13], but they have recently been confirmed in an independent study[14]. We have used Walch's calculations as the basis for developing a global analytical surface for HNNO. This surface uses a many-body expansion to describe two and three body forces, based on N_2O, HNO and HN_2 surfaces that we developed earlier. The full HNNO surface has been adjusted to fit Walch's minima and saddle point energies for reactions (1 and 2) to within 1 kcal/mol, and to fit qualitatively the reaction path profiles for the two different pathways associated with production of N_2 + OH.

We have now completed reaction dynamics studies of reactions (1) and (2) based on our fitted HNNO surface, and we are continuing to do calculations based on the van der Waals counterpart to (2). Our results for reaction (1) are described in attached reprints[15,16], so we only give a brief summary of the results here. We find from both trajectory and RRKM calculations that the branching between reactions (1a) and (1b) is such that (1a) accounts for 10-15% of the reaction at low temperature. This result is very close to several recent determinations, including 20% from Durant[14], 14% from Bozzelli and Dean[11], 15% from Volpp and Wolfrum[17], and a revised value of 27% from Okada and coworkers[18]. We have further demonstrated that our branching fraction does not change significantly as the two barriers responsible for decay of HNNO into the products of reactions (1a) and (1b) are varied within a few kcal/mol.

Our product energy partitioning results[19] are also interesting. Reaction (1a) is strongly exoergic (98 kcal/mol), but very little is known about where this energy is deposited in the product degrees of freedom. Dagdigian[7] finds that the OH product vibration and rotation are only slightly excited, and our results are consistent with these findings. We find that most of the available energy (>70%) ends up in product translation, with the N_2 vibration and rotation being only modestly excited. A similar result occurs for reaction (2a) when compared at the same energy as (1a), as makes sense given that the same 1,3 hydrogen migration pathway is involved in both reactions. However our result for reaction (1a) is seriously at odds with recent measurements due to Wittig and coworkers[6,8], who used Doppler profile measurements on the OH product to infer information about the translational distribution. Wittig's results indicate (indirectly) that N_2 vibration and/or rotation receive most of the available energy (60%). Wittig has justified this surprising result based on a simple model which looks at the change in N-N bond distance that accompanies hydrogen migration. However, we have incorporated this N-N distance change into our surface, and yet we do not find results that are consistent with his simple model. In addition, we find that reaction (1a) is dominated by an alternative reaction mechanism in which H adds directly to the O end of NNO, for which there is virtually no N-N bond distance change during reaction. This mechanism is assumed not to happen in Wittig's model even though the barrier for reaction is well below the energy available for reaction.
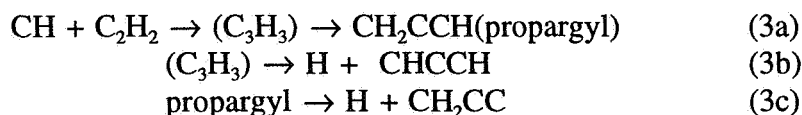
Our results for H + N_2O[19] indicate that the previous attempts[9-11] to model the kinetics of reaction 2a were incomplete. After modest (1 kcal/mol) lowering of the barriers for migration and for oxygen abstraction, our trajectory rate constants are in good agreement with experiment[9]. This agreement is obtained without including tunnelling and without including

for pressure effects (in other words, in the low pressure limit). We further find that the HNNO intermediate complex lifetime is sufficiently short (~ 1ps) for reactions that contribute to the thermal rate constant that collisional effects are likely to be minor at the pressures considered in the experiments (100-300 Torr). Our results show that the indirect mechanism (HNNO formation) is dominant at low temperatures while the direct mechanism (O abstraction) is dominant at high temperatures. The difference is activation energies between these two mechanisms is about 3 kcal/mol, which is enough to accommodate the observed temperature dependence. The previous studies omitted the direct mechanism, and therefore had to make up for its absence by invoking other mechanisms for producing strong temperature dependence to the effective rate constant.

(2) Modelling Soot Precursor Formation

A newer project that we have been working on concerns the production of soot precursor molecules in acetylene combustion. Previous theoretical work by Miller and Melius[20] postulated that a primary route to the production of benzene and then to polycyclic aromatic hydrocarbons involves dimerization of the propargyl radical CH_2CCH. One route to the product of propargyl is the reaction of CH with acetylene, followed by collisional stabilization. Another route is the reaction of $^1CH_2$ with acetylene followed by H atom emission. There have been no experimental studies of CH + C_2H_2 that we are aware of, but two studies of $^1CH_2$ + C_2H_2[21,22]. In the $^1CH_2$ + C_2H_2 experiments, only the overall rate of loss of $^1CH_2$ was determined (3 x 10^{-10} cm^3/s), so what is unknown at this point is the branching between electronic quenching (for form $^3CH_2$) and several possible reactive products.

Walch[23] has recently used high quality *ab initio* methods to characterize the potential surface of both of these reactions in detail. He finds that for CH + C_2H_2, the reaction mechanism that can roughly be summarized as follows:

$$CH + C_2H_2 \rightarrow (C_3H_3) \rightarrow CH_2CCH(propargyl) \qquad (3a)$$
$$(C_3H_3) \rightarrow H + CHCCH \qquad (3b)$$
$$propargyl \rightarrow H + CH_2CC \qquad (3c)$$

In this mechanism, (C_3H_3) stands for one or more intermediates (typically with H's attached to each carbon) that are found on the way to propargyl. Both products have the formula C_3H_2, but CHCCH, which is produced by H emission from (C_3H_3), is about 1 kcal/mol more stable than CH_2CC, which comes from propargyl. Walch finds that the (C_3H_3) isomers can dimerize to benzene even more easily than can propargyl, so his calculations open up the possibility that species other than propargyl may be significant in the formation of benzene and similar molecules. However propargyl is more stable than the (C_3H_3) isomers, so the relative importance of these isomers depends on details of the CH + acetylene reaction kinetics that are not available from Walch's calculations without further work.

We have used RRKM theory to calculate the overall rate of reaction (3) as well as the unimolecular lifetimes of (C_3H_3) and propargyl. Since there is no barrier for addition of CH to C_2H_2, we have used variational RRKM theory to determine the rate constant. Walch has kindly calculated structures and energies (CASSCF for structures, CASSCF + ICCI for

energies) along the reaction path leading from the reagents to the (C_3H_3) minimum, which enables us to determine variational transition states with reasonable precision. At the present time we have interpolated the vibrational frequencies along the reaction path, but Walch plans to generate these as well, which would eliminate the only serious source of uncertainty in our results. We find that the overall reaction rate (high pressure limit) is 6.1×10^{-10} cm^3/s at 300K, which if correct makes $CH + C_2H_2$ about twice as fast as its $^1CH_2 + C_2H_2$ counterpart. We also find that the (C_3H_3) intermediate complexes have unimolecular decay lifetimes of at most 1 ps, while the corresponding propargyl lifetime is 6 ps, so it seems likely that propargyl will be the dominant collisionally stabilized product. Even this lifetime is too short for propargyl to be stabilized under many circumstances, so we expect the reaction will proceed on to C_3H_2. The dominant form of this molecule is predicted to be CH_2CC. The chemistry of this species has so-far not been characterized, so an important follow-up to the present project would be to study the reactions of this species.

Walch's calculations on the $^1CH_2 + C_2H_2$ reaction indicate that the primary reaction pathways are:

$^1CH_2 + C_2H_2 \rightarrow$ (cyclopropene) ⇌ (propyne or allene) $\rightarrow$ H + propargyl
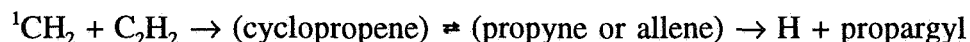
The isomerization of allene to propyne via an intermediate cyclopropene is a reaction mechanism that has previously been characterized[24]. Walch's calculations show that $^1CH_2 + C_2H_2$ feeds directly into this same reaction mechanism, which means that propyne and allene are intermediates that can be formed in the $^1CH_2 + C_2H_2$ reaction. Further, it is the emission of H atoms from allene and propyne that is responsible for propargyl production.

We have used Walch's results, plus additional calculations that he has provided, to estimate the high pressure rate constant for $^1CH_2 + C_2H_2$, as well as unimolecular lifetimes of the various intermediates. Again there is no barrier to reaction, so we have used variational RRKM. We do not yet have vibrational frequencies along the reaction path, so interpolation is also necessary. In this case our best current estimate of the rate constant at 300K is 7×10^{-11} cm^3/s, which is a factor of 4 below experiment[21,22]. The error here is comparable to the uncertainty associated with the frequency interpolation, so it is too early to tell if there is a significant discrepancy with experiment. Another potentially important issue is that the experimental result refers to the sum of rate constants for reaction and for electronic quenching. If quenching is fast sufficiently fast, it is possible that both theory and experiment are correct as they now stand.

Our calculations of unimolecular decay lifetimes indicate that propyne has nanosecond lifetimes. Allene's lifetimes are about a factor of 10 below propyne. These long lifetimes mean that there should be considerable pressure dependence to the reaction rate, and in fact it is possible that under typical combustion conditions propyne and allene rather than propargyl, are the major products of the reaction between singlet methylene and acetylene.

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